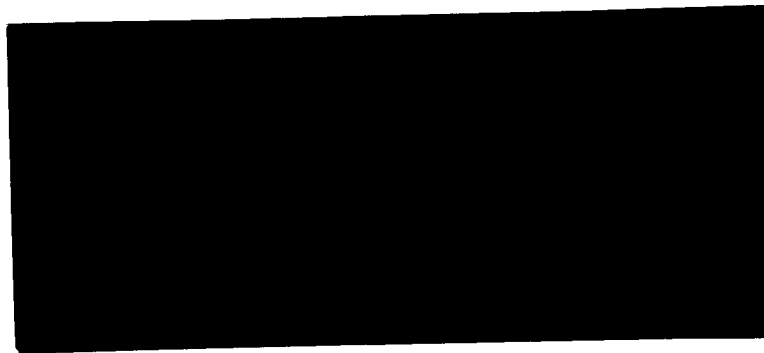


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INVESTIGATION OF
BATTERY ACTIVE NICKEL OXIDES

BY

P. Ritterman and H. N. Seiger

Prepared For
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
CONTRACT NAS 3-7620

GULTON INDUSTRIES, INC.
Alkaline Battery Division
Metuchen, New Jersey

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SECOND QUARTERLY REPORT

INVESTIGATION OF BATTERY ACTIVE
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P. Ritterman and H. N. Seiger

Prepared For
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

December 12, 1965

CONTRACT NAS 3-7620

Technical Management
NASA Lewis Research Center
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SUMMARY

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X-ray studies of sintered plate nickel oxide electrodes indicated that no noticeable structure change occurs until the electrode is at least 75% charged. This was true for both the C/2 and C/10 rate.

Electrodes impregnated with nickel nitrate containing 20 metal atom percent of cobalt have been tested. These appear to have better charge retention characteristics at elevated temperatures. The utilization of active material (based on weight gain) is also quite high.

Three groups of positive electrodes have been given three formation cycles, with the following conditions: (1) 10°C at C/30, (2) 80°C at C/10, and (3) 25°C at C/10, the first two groups having previously been shown superior on stand; the last group serving as a control.

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INVESTIGATION OF
BATTERY ACTIVE NICKEL OXIDES

by

P. Ritterman and H. N. Seiger

ABSTRACT

X-ray diffraction patterns are shown which indicate that no structural difference exists between a discharged and 0.75 charged sintered positive electrode. This is shown to be true at both the C/2 and C/10 rates.

Ten plates impregnated with nickel nitrate containing 20 metal atom percent of cobalt were prepared. Superior charge retention at 65°C was shown by these plates. Utilization was in excess of 100% of theoretical capacity.

Freshly impregnated sintered nickel oxide plates were formed in three groups of ten, at C/30 and 10°C, C/10 and 80°C, and C/10 and 25°C.

I. INTRODUCTION

A. PURPOSE

Investigations performed under this contract include the following: (1) identification and characterization of materials formed at the positive electrode of a sintered Ni-Cd cell at various temperatures and states of charge; (2) various means of stabilization of the positive electrode material at elevated temperatures; and (3) studies of the utilization, efficiency, voltage, and cycling characteristics of the positive electrodes which have been improved by stabilization.

B. STATUS OF PROGRAM AT THE BEGINNING OF THE QUARTER

During the quarter ending September 12, 1965, investigations concerning the composition of the positive electrode were done primarily by X-ray technique. It was shown that more meaningful results were obtained by X-raying a plate without a polyethylene cover. Using these data as a means of determining structure and composition, as related to state of charge, was theorized. Chemical analysis was developed to the point where the formula weight of active material in the sintered positive electrode could be determined at various states of charge.

A study of the effects of formation at various rates and temperatures revealed that the least capacity loss occurred on stand in cells whose positives were formed at 100 ma and 80°C and 35 ma and 10°C.

C. MEETINGS

On December 7, 1965, a meeting was held with Mr. W. Nagle of NASA/Lewis. Dr. H. N. Seiger and Mr. R. Michaels represented Gulton Industries. Dr. P. Vaughan of Rutgers University, consultant for Gulton Industries, was also present. The meeting took place at Gulton Industries, Metuchen, N. J. The discussion centered around the First Quarterly Report, as well as a work plan for future experimentation.

The discussion of future work included the decision to form and evaluate the plates impregnated with additives at a 20% dopant level. It was further decided to synthesize and analyze oxides of nickel whose valence was in excess of three (3), using techniques described in a recent publication.

Dr. Vaughan discussed his theory of the structural changes which occur at the positive electrode during charge and discharge.

II. OUTLINE OF PROGRAM

The program is divided into two parts. The first involves a continuation of the investigation into the qualitative and quantitative nature of the sintered nickel oxide electrode, begun under Contract No. NAS 3-4178. This investigation will be carried out by the use of chemical, electrochemical, and X-ray diffraction techniques as methods of analysis. The second part will concern itself with methods of stabilizing the nickel compounds formed during charge of the positive electrode. The stabilization methods used include: (1) additives (the inclusion of foreign materials within the structure of nickel oxide crystals; (2) formation at various currents and temperatures; and (3) any other means of nickel oxide stabilization deemed feasible will be presented for approval to the NASA Project Manager. Plates made by these methods have been, and will be, evaluated with respect to retention of charge on stand, and performance on charge and discharge (4 cycles).

A. IDENTIFICATION AND CHARACTERIZATION OF BATTERY ACTIVE MATERIAL EXISTING IN THE NICKEL OXIDE ELECTRODE.

1. Construction of Test Cells

a. Plates

Positive plates were used, all of which were impregnated at the same time with $\text{Ni}(\text{NO}_3)_2$ and then chemically converted to $\text{Ni}(\text{OH})_2$.

b. Stacks

Single positive plates were surrounded by excess negative capacity in the form of two sintered cadmium electrodes with two layers of non-woven nylon serving as separator and 34% KOH as electrolyte.

2. Formation Treatment

Thirty cores were constructed and cycled using the following regime:

- a. Charge at C/10 for 16 hours.
- b. Discharge to 0 volts at C/3.
- c. Short for 2 hours.

This was repeated 3 times. Twenty cells most alike in capacity were chosen for further testing.

3. Effect of State of Charge and Rate of Charge

- a. After the third formation cycle was completed, 10 cells were charged at C/2 for 4 hours.
- b. Two cells were discharged at C/2 for 1 hour.
- c. Two cells were discharged at C/2 to 1.0 V.
- d. Two cells were discharged at C/2 for $\frac{1}{2}$ hour.
- e. Two cells were allowed to retain their fully charged state.
- f. Two cells were charged to the gassing point of the positive plate.

After a 24 hour stand on open circuit, the cells were taken apart and the positive plate analyzed by X-ray diffraction and electrochemical means.

Steps a. to f. were, in part, carried out at the C/10 rate.

4. Stand Time at Various Temperatures

After preparing 24 cells chosen from 30 (those most alike in capacity), they will be charged at C/10 for 20 hours at room temperature. Twelve of the cells will then be disassembled immediately and the positives placed in beakers of 34% potassium hydroxide. The remaining 12 cells will remain as they are. Four disassembled cells and four assembled cells will be placed in an oven at 50°C. A like number of cells will be placed in a cold box at 10°C, and the remaining cells will be kept at 25°C. After 24 hours, two disassembled positives, along with two positives from the assembled cells, taken from each temperature stand, will be analyzed. The remaining positives and cells will stand at their respective temperatures for three months and then be analyzed.

5. Methods of Analysis

The plates will be analyzed by X-ray diffraction and chemical and differential thermal analytical means.

a. Chemical Means

Emphasis will be placed on chemical analysis for quantitative determination of Ni, H, and O in the active portion of the plate.

(1) Nickel

In a sintered plate, the interference of pure nickel must be eliminated. Total nickel can be determined by

electroplating or precipitation in alkaline solution as nickel dimethylgloxime.

Methods for separating Ni^0 from the divalent, trivalent, or tetravalent nickel oxides will be explored. Determination of the amount of Ni^0 present in an impregnated sintered plaque will also be explored.

(2) Hydrogen

A washed and dried sample will be mixed with K_2CrO_4 and PbCrO_4 and heated to 600° . The water vapor then produced will be captured in a weighed drying tube.

(3) $\text{Ni}^{+2}/\text{Ni}^{+3}$

Methods will be sought to determine the amount of $\text{Ni}^{+2}/\text{Ni}^{+3}$ present in a particular sample.

(4) Oxygen

Oxygen can best be determined by difference, with respect to the total nickel and hydrogen determined.

b. X-ray Diffraction

(1)
As was stated in the Final Report; the possibility of X-raying a wet positive without polyethylene covering has been further examined. The plate was kept in polyethylene until just before mounting it into the goniometer. The plate was wet with KOH and, in essence, was identical with the plate within the cell. The duration of one X-ray sweep is less than 40 minutes and during that time interval the viscous KOH did not dry out.

All X-ray diffraction after the first quarter was done with uncovered samples, and we shall continue to do so.

c. Differential Thermal Analysis

The plate sample will be ground into a powder and placed in a stainless steel block containing 3 thermocouples. Another hole in the block contains powdered alumina. The thermocouples are so arranged that there is a response to any reaction or transitional change of the sample. The question of obtaining standards besides $\text{Ni}(\text{OH})_2$ remains the difficulty.

(1) See References, Page

B. STABILIZATION OF NICKELIC OXIDES AND HYDROXIDES

1. Formation at Various Temperatures and Rates

Cells will be constructed using one unformed sintered positive surrounded by two negative plates. As described in previous sections, formation will be performed at the C/2, C/10, and C/30 rates and at temperatures of 10⁰, 25⁰, and 80⁰ for each rate. Three cells will be formed at each rate and each temperature for 3 cycles.

2. Additives

Impregnating nickel solutions will be prepared containing 5%, 10%, and 20% metal atoms of Co, Ba, and Mn. These elements are near nickel in the periodic table. Alkali and alkaline earths will include Li, Mg, Na, Be, and Ca. These will be incorporated by use as the salt of the nitrate ion. A control solution of pure nickel nitrate will also be used.

For each quantity and additive type, 10 plates will be impregnated. These will be formed by standard methods or by the procedure found to yield optimum results.

3. Other Techniques of Stabilization

Other means besides the vacuum impregnation used by Gulton Industries will be explored. These will include molten salt impregnation and anodic as well as cathodic impregnation of sintered plaques from dilute solutions of nickel salts.

The impregnation method with which we are familiar, by previous experience, involves the impregnation of a sintered nickel plaque made cathodic in a solution of dilute nickel nitrate. It has been found that nickel-cadmium cells made from plates of this type have performed very well at elevated temperatures.

C. PRELIMINARY EVALUATION

Electrodes stabilized by the above described methods will and have been evaluated in the following manner.

1. Storage and Evaluation

At least three cells of each group will be constructed. The capacity will be determined as follows:

- a. C rate charge for 2 hours.
- b. Immediate discharge at C/5 to 0.0 V.

The charge will be repeated and after various stand times at several temperatures, the cell discharged at C/5 to zero volts.

This was done at 50°C, 40°C, and 65°C. A check of capacity on immediate discharge at room temperature will be made before each stand test.

2. Electrochemical Stabilization Tests

Samples of each group shall be cycled for 4 cycles at C/10 charge--C/5 discharge at room temperature. Methods of evaluation include capacity, reproducibility of results with respect to capacity, efficiency and voltage level.

D. EVALUATION OF IMPROVED MATERIAL

After establishing a superior material or a group of superior materials with respect to stabilization, the following tests will be made.

1. Decomposition of Charged Positive

Using 15 cells consisting of the superior material with respect to stabilization, the following tests will be performed.

Cells will be allowed to stand at temperatures of 20°, 40°, 60°, 80°, and 95°C, and after a passage of 1 day, removed, discharged at the C/5 rate to a 1.0 V end point at room temperature. The capacity of all cells will be determined immediately after charge at the C rate. This will be repeated by charging the same cells at the C rate and extending the stand time to 3 days. The test will be repeated allowing just the charged positive plates to be immersed in electrolyte at the various temperatures, the capacity of which, again, will have been previously determined. These plates will then be surrounded by negatives and discharged to 1.0 V at the C/5 rate. This, too, will be repeated extending the charged stand time if significant differences are noted between the 1 and 3 day stand.

2. Investigation of Sintered Plate parameters

After establishing a loading factor which meets the approval of the NASA project manager, the following investigation will be made.

a. Establishment of Optimum Formation Technique

The optimum formation shall be considered to be the one which produces a plate which, when incorporated into cells, yields the highest voltage level on discharge, the greatest capacity per unit weight and volume, optimum charge efficiency, and most consistent reproducibility of the aforementioned results.

A statistical experiment involving rate, amount of over-charge, and number of cycles will be used to establish optimum

conditions. Before such an experiment is begun, past experience tells us that an initial low rate charge and discharge cycle at the C/10 rate or less should be used.

b. Establishment of Charge acceptance as a Function of Charge Rate, and Determination of Point of Oxygen Evolution at Various Rates.

The characteristics of positive plates can be established with one experiment. A positive plate is contained in a sealed chamber of known volume together with an oxygen consuming electrode. Both the oxygen electrode and the positive plate have external connections allowing for charge. The sealed chamber is filled with pure oxygen and a pressure gauge records oxygen pressure. As current is passed to charge the positive plate and cause oxygen reduction at the appropriate electrode, the rate of oxygen pressure decay should be in direct proportion to the charging current provided that no oxygen is produced at the positive. The deviation from the theoretical slope will not only establish the charge acceptance, but will also indicate the point at which oxygen evolution begins. This can be established for the one, two, five, and ten hour rates.

c. Determination of Utilization Factors at Various Rates of Discharge.

The three plate cells, consisting of 1 positive and 2 negative electrodes, will again be employed here. All charges will be done at the 1 hour rate. Discharges will be performed at the 10 minute, 1 hour, two hour, 5 hour, and the 10 hour rates. Capacities will be determined to 1.0 V and also the point just before the graphitic level.

d. Determination of Utilization Factors for Depth of Discharge at 25%, 35%, 50%, 75%, and 100%

A group of three plate cells will be charged at the C rate. After the initial charge, the cell will be discharged for 15 minutes at the C rate. It will then be charged for 15 minutes at the C rate and finally discharged to 1.0 V at the C rate. This will be repeated for a 21 minute discharge, a 30 minute discharge, and similarly to obtain the other stated depths of discharge. A comparison will be made of the capacities obtained when discharging to 1.0 V versus the various depths of discharge. This will be done for other charge rates as well.

III. EXPERIMENTAL PROCEDURES AND RESULTS

A. EXPERIMENTAL PROCEDURES

1. Determination of Battery Active Materials Existing in the Sintered Plate Nickel Oxide Electrodes

a. Effect of State of Charge and Rate of Charge

(1) Construction of cells

Thirty cells consisting of 1 positive and 2 negatives were assembled as described in Section II. Each positive plate had the dimensions of $1\frac{7}{8} \times 2\frac{1}{8} \times .035''$ and contained 3.4 grams of Ni(OH)_2 .

(2) Formation Procedure

All cells were charged at 100 ma for 16 hours and discharged immediately at 400 ma to 0.0 V. Upon completion of discharge, cells were shorted for 2 hours. This procedure was repeated twice more.

(3) Selection of Cells and Test Procedures

Based on the capacity of the third formation cycle, 20 cells were chosen for further testing. Six of the 20 cells were charged at 500 ma for 4 hours. Two of these were discharged at the same rate for $\frac{1}{2}$ hour. Two others were discharged at 500 ma to 1.0 V. The remaining two cells were kept at their fully charged state.

All six cells stood on open circuit for a period of 24 hours after which time they were disassembled and their positives placed in separate polyethylene bags. Just before being placed in the goniometer of the X-ray diffraction apparatus, each positive was removed from its polyethylene container. Thus, X-ray diffraction patterns were obtained from plates wet with KOH and uncovered.

Six other plates were charged at 100 ma for period of 20 hours. Two were discharged at 100 ma for $2\frac{1}{2}$ hours; two were discharged at the same rate to 1.0 V; and two retained their fully charged state. Upon completion of their electrochemical treatment, all six cells were disassembled, their positives placed in polyethylene bags which were removed before X-ray diffraction patterns were taken.

The goniometer was set at 2° per minute chart speed at 30"/hr. for all X-ray determinations.

The remaining eight cells were set aside for future testing.

b. Chemical Determination of Active Nickel in Sintered Plates

Unimpregnated sintered plates were allowed to stand in heated solutions of $\text{NH}_4\text{OH}-(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\text{NH}_4\text{OH}-(\text{NH}_4)_2\text{SO}_4$, and $\text{NH}_4\text{OH}-\text{NH}_4\text{AC}$ for a period of 1 hour in the first two mixtures and 4 hours in the third. The weight of the sintered plates before and after treatment was determined.

2. Stabilization Studies

a. Formation

(1) Construction of Test Cells

30 cells were constructed as described in Section A.1.a.(1).

(2) Formation Procedure

Cells were formed in groups of 10 at 100 ma at 25°C, 35 ma at 10°C, and 100 ma at 80°C. The charge at each rate was of such duration as to equal 150% of the theoretical capacity of the cell, which amounted to 15 hours for the 100 ma charges and 45 hours for the 35 ma charges. The discharge was to zero volts, followed by a minimum of a 2 hour short.

Cells received 3 formation cycles.

b. Additives

(1) Impregnation of Sintered Plates

10 sintered plates, 1-7/8 x 2-1/8 x .035" were vacuume impregnated with nickel nitrate solution containing 20% of Co^{2+} . Conversion to hydroxide was done in 25% KOH at 70°C. Impregnation was repeated until plates had gained approximately 3 grams.

(2) Construction of Test Cells

Thirteen test cells were prepared using the standard three plate cell technique.

Ten of the cells were prepared using cobalt containing positives and three using the standard positive. The positives were wrapped in a single layer of separator to prevent shorting with the negative on disassembly.

(3) Formation

The cells were given three formation cycles at 100 ma at room temperature.

(4) Tests and Evaluation

(a) Capacity retention on stand

Six of the cells containing cobalt doped positive plates and three control cells containing Gulton positive plates were charged at 100 ma for 16 hours and then discharged at 500 ma to 0.0 V. After discharge cells were shorted for 2 hours and then again charged at 100 ma for 16 hours.

After charge, the positives were removed from the cells. One control and two cobalt positives were stored at 25°C, 40°C, and 65°C. Each positive was stored in a separate beaker of potassium hydroxide. After a two day stand at temperature, one cobalt plate from each temperature was returned to its particular antipode cell case, thus remaking the original cell. The three cells were discharged to zero volt at 500 ma. After 7 days in their ambient the remaining 3 cobalt doped plates and the 3 controls were returned to their negatives and cell cases and then discharged at 500 ma to zero volt.

(b) Cycling Properties

Four cells with cobalt containing positives were charged at 100 ma for 16 hours and then discharged at 200 ma to 0.0 volt. The cells were then shorted for two hours. This was repeated twice more.

B. EXPERIMENTAL DATA

1. Determination of Battery Active Materials Existing in the Sintered Plate Nickel Oxide Electrode

a. Effect of State and Rate of Charge

(1) Formation

The discharge capacities obtained during formation of the 30 sintered plates are shown in Table I. The check marks indicate the 20 cells chosen for further testing.

(2) Preparation For and X-ray Analysis of Positive Plates at Various States of Charge

(a) C/2 Rate - The six cells used for this test were numbers 7, 8, 9, 10, 11, and 12. Cells 7 and 8 were left fully charged and the X-ray diffraction pattern obtained from their positives is shown in Figures 1 and 2 respectively. Cells 9 and 10 were discharged for $\frac{1}{2}$ hour (C/2 rate) and the X-ray patterns from their $\frac{3}{4}$ charged positives are shown in Figures 3 and 4. The remaining two cells were discharged to 1.0 V (C/2 rate), cell number 11 requiring 123 minutes and cell number 12 requiring 125 minutes to reach that voltage. Figure 5 and 6 are the respective X-ray diffraction patterns obtained for these positive electrodes.

(a) C/10 Rate - Cell numbers 22, 23, 24, 25, 26, and 27 were used for this test. The patterns obtained from the positives of these cells appear in Figures 7 through 12 respectively. Cells 24 and 25, which were discharged to 1.0 V, required 10 hours and 28 minutes and 9 hours 22 minutes, respectively, to reach their required voltage. Cells 22 and 23 were discharged $2\frac{1}{2}$ hours and the remaining two cells retained in the fully charged state.

The major peaks and their intensities are shown in Table II for both rates.

b. Chemical Determination of Active Nickel in Sintered Plates

Unimpregnated sintered plates were allowed to soak in mixtures of ammonium hydroxide and ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$, ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$, and ammonium acetate (NH_4OAc) . The results are as follows.

<u>MIXTURE</u>	<u>SOAKING TIME (Hrs.)</u>	<u>WT. LOSS OF NICKEL SINTER (gms)</u>
$\text{NH}_4\text{OH}-(\text{NH}_4)_2\text{S}_2\text{O}_8$	1	0.0252
$\text{NH}_4\text{OH}-(\text{NH}_4)_2\text{SO}_4$	1	0.0048
$\text{NH}_4\text{OH}-\text{NH}_4\text{OAc}$	4	0.0027

As can be seen from the above data, the last mixture should be used to remove the active nickel from an impregnated plate since it interacts least with the nickel sinter.

2. Stabilization

a. Formation

The discharge capacities obtained from the cells used in this experiment during formation at 25°C-100 ma, 70°C-35 ma, and 80°C-100 ma are shown in Table III for all three discharge cycles.

b. Additives

(1) Impregnation and Formation

The weight gains of the 10 plates impregnated with nickel nitrate containing 20 metal atom percent cobalt are shown in Table IV. The capacity obtained to 1.0 V and 0.0 V on the third formation cycle is also shown.

(2) Stand and Cycling Test

The capacities of six cobalt plates along with three control plates appear in Table V. The control plates made with pure $\text{Ni}(\text{NO}_3)_2$ solution had the same formation history as the cobalt plates.

The table also shows the capacities obtained from the three cobalt plates after charged stand for 2 days at room, 40°C and 65°C; Cb-5, Cb-2, Cb-4 respectively. The loss of capacity to 1.0 V on the two day stand, as compared to immediate discharge was 5% at room temperature, 10% at 40°C, and 7% at 65°C. Cobalt plates Cb-10, Cb-1 and Cb-3 stood charged on open circuit for 7 days at room, 40°C and 65°C respectively. C-1, C-2, and C-3 also stood on open circuit at these temperatures in the same respective order. At room temperature, both control and cobalt doped plates lost 9% of capacity on stand. At 40°C, 15% of capacity was lost by both control and cobalt plates. At 65°C, however, the cobalt plate lost 15% while the control plate lost in excess of 50% of capacity. The percentage loss to zero volts did not vary significantly from the loss to 1.0 V, except in the case of the control plate at 65°C where capacity loss to zero volts was 35%.

The capacities to 1.0 V and 0.0 V obtained on discharge of the 4 cells containing cobalt doped positives Cb-9, Cb-7, Cb-6, and Cb-8, for the 4 formation cycles, are shown in Table VI. The capacities were reproducible from cycle to cycle and averaged slightly above their theoretical capacities (based on weight gain).

A typical discharge curve is shown in Figure 13.

C. DISCUSSION

1. Determination of Battery Active Material Existing in the Sintered Plate Nickel Oxide Electrode

a. Effect of State and Rate of Charge

The "d" spacings, as shown in Table II, again indicate the, at least partially, disordered arrangement of the charged state of the nickel oxide electrode. The only definite peak which is retained is the charged state occurring at "d" = 4.60-4.70 Å. This can be explained as a lateral shift of oxygen layers caused by the weakening of the interlayer bonds due to the loss of hydrogen on charge. The stand of 24 hours, given to the cells which received high rate (C/2) charge, accounts for the absence of any peaks due to unstable compounds. At both the high and low rate of charge, there were no significant differences in the peak intensities and, further, the areas under the peaks, for the two plates that were one-quarter discharged, were not significantly different from the areas under the peaks of the plates that were fully discharged to 1.0 V.

The X-ray patterns found corresponded to the hexagonally close packed structure of Ni(OH)_2 . From this, one would assume that even in the one-quarter discharged state, a sufficient number of protons had returned to the lattice to cause the interlayer bonding and reestablish the Ni(OH)_2 structure.

Another explanation of the similarity of structure and intensity at various states of charge, is the extent of surface penetration of X-rays into the crystals of the nickel oxide which exist in the pores of the sintered nickel electrode.

A calculation revealed that the depth of penetration corresponding to 95% of the diffracted intensity was many orders of magnitude greater (0.01") than the expected size of a crystal. This eliminates the possibility of the partially discharged surface of a crystal of active material accounting for the similarity of patterns obtained from 75% charged and completely discharged electrodes.

The thickness of the sintered plate is 0.035". The grid material is 0.01" thick, leaving the sintered nickel and active material with a thickness of .013" for each side. For a mixture of nickel and of active material, the depth of penetration which yields 95% diffraction, corresponds to slightly less than 0.01" but certainly more than .003". Since we are dealing with a porous material, the penetration probably exceeds .01". The remote possibility of discharged material existing within the depth of the sintered plate as a cause of the patterns is thus negated.

Further study is being made by examining individual peaks at low scanning speeds to obtain their relation to state of charge. The data thus far obtained indicates little structural change until some point between 75% charged and fully charged. The effect of rate between these two states would be of great interest.

b. Chemical Determination of Active Nickel in Sintered Plate

The results indicate that a mixture of NH_4OAC and NH_4OH is superior in that its reactivity with the nickel sinter is negligible.

2. Stabilization

a. Formation

The capacities obtained during formation of the 10 cells cycled at 35 ma and 10°C were higher than the groups cycled at the other temperatures and rates.

b. Additives

The results of stand tests indicate that positives impregnated with nickel nitrate containing cobalt are considerably superior to undoped positives, with respect to retaining capacity at elevated temperatures. Cycling tests have also indicated the utilization, voltage level and reproducibility of capacity of such plates to be satisfactory (see Tables V and VI). Further tests with respect to charge retention at elevated temperatures are now being conducted.

IV. CONCLUSIONS

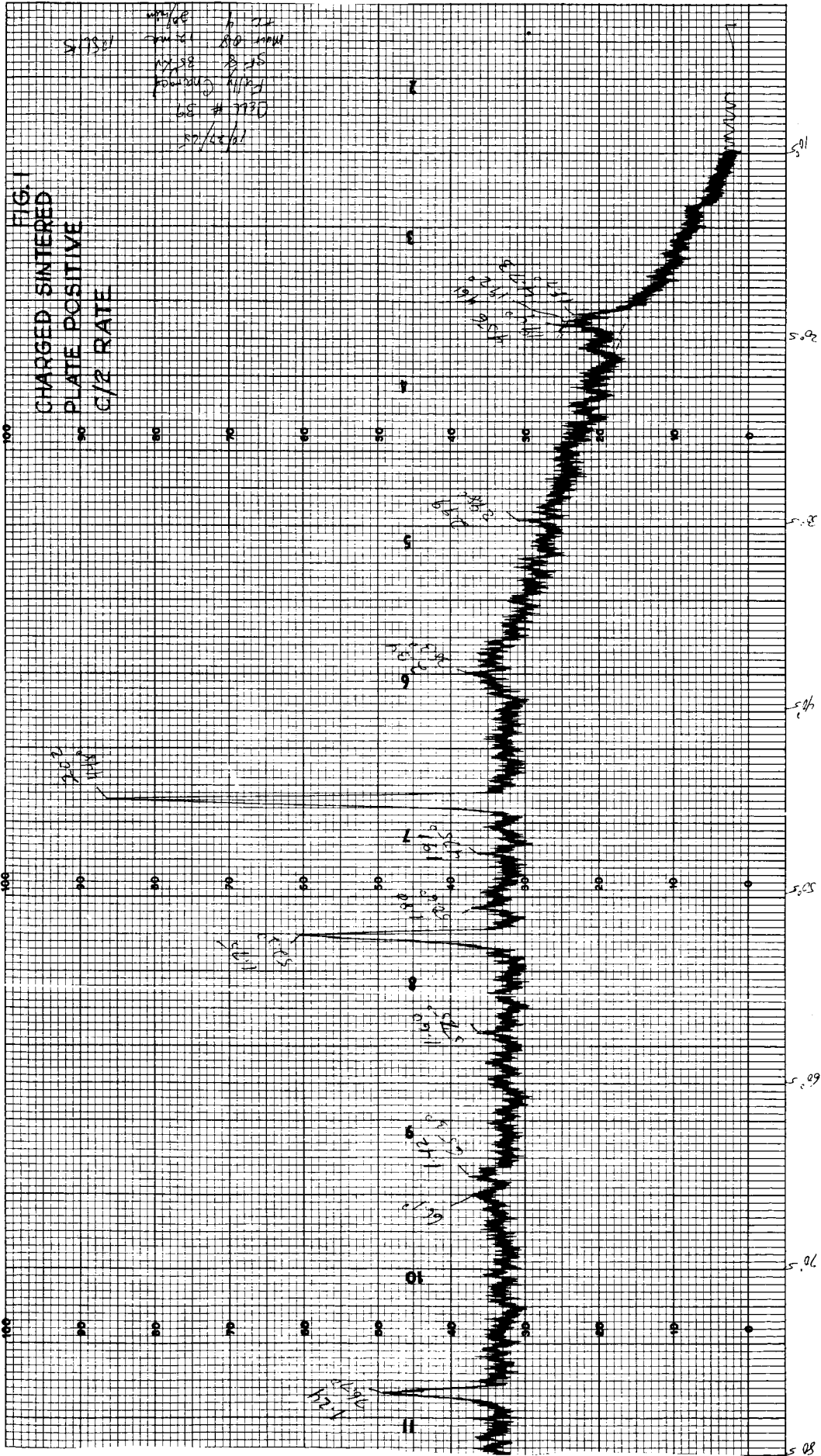
1. There is no structural change in the active material of the sintered nickel oxide electrode until the plate is at least 75% charged.
2. Cobalt doped positives are superior with respect to undoped positives at elevated temperatures.

V. FUTURE WORK

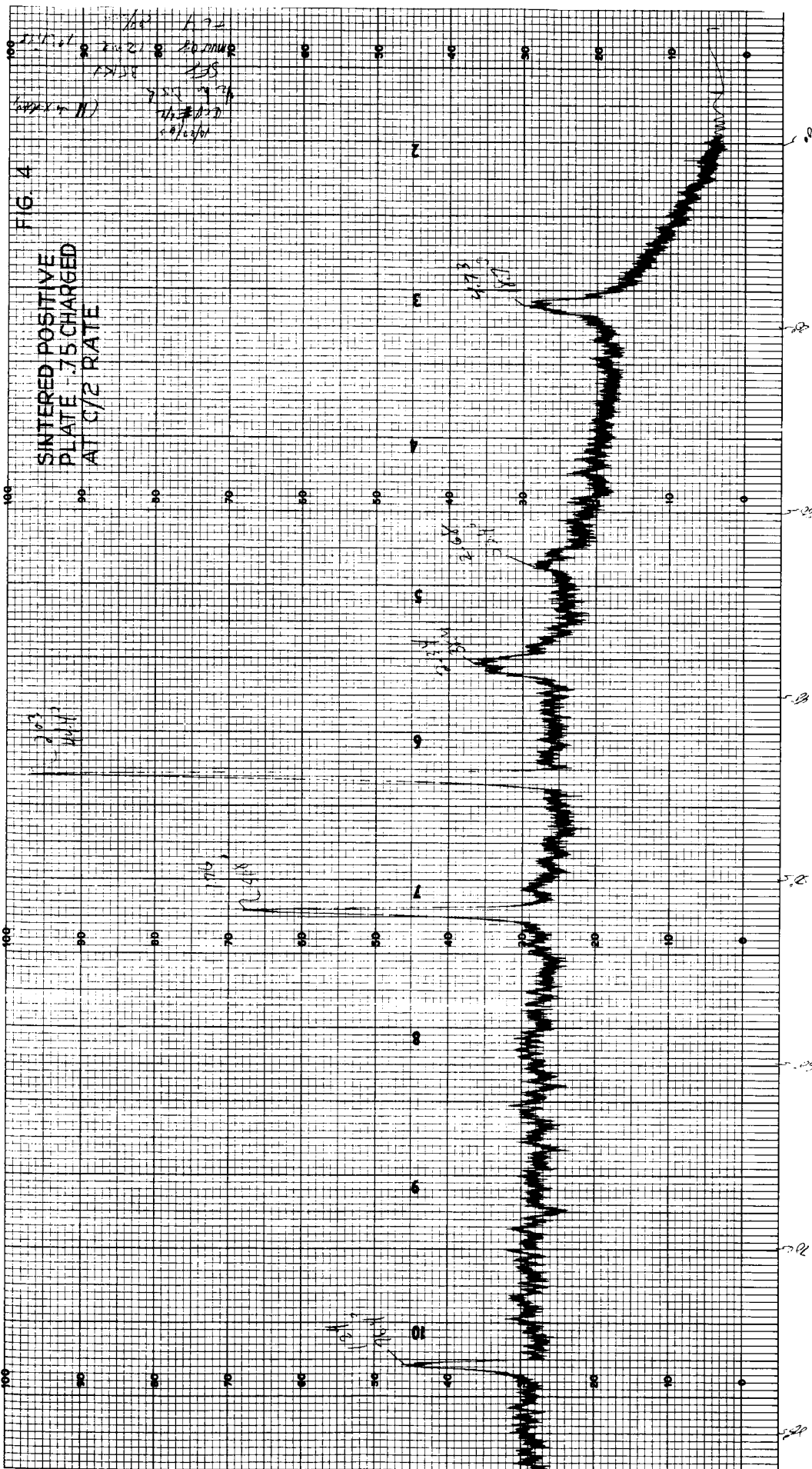
1. Evaluation of formation as an effective means of producing improved positive electrodes will continue.
2. Additives in a 20% basis will be evaluated.
3. Cobalt, which shows promise, will be investigated further with regard to charge retention.
4. High valence nickel oxide compounds will be prepared by chemical oxidation.
5. A low scan rate of the goniometer, combined with low chart speed will be used to obtain X-ray diffraction patterns at various states of charge.
6. Chemical analysis of the oxides will be continued.

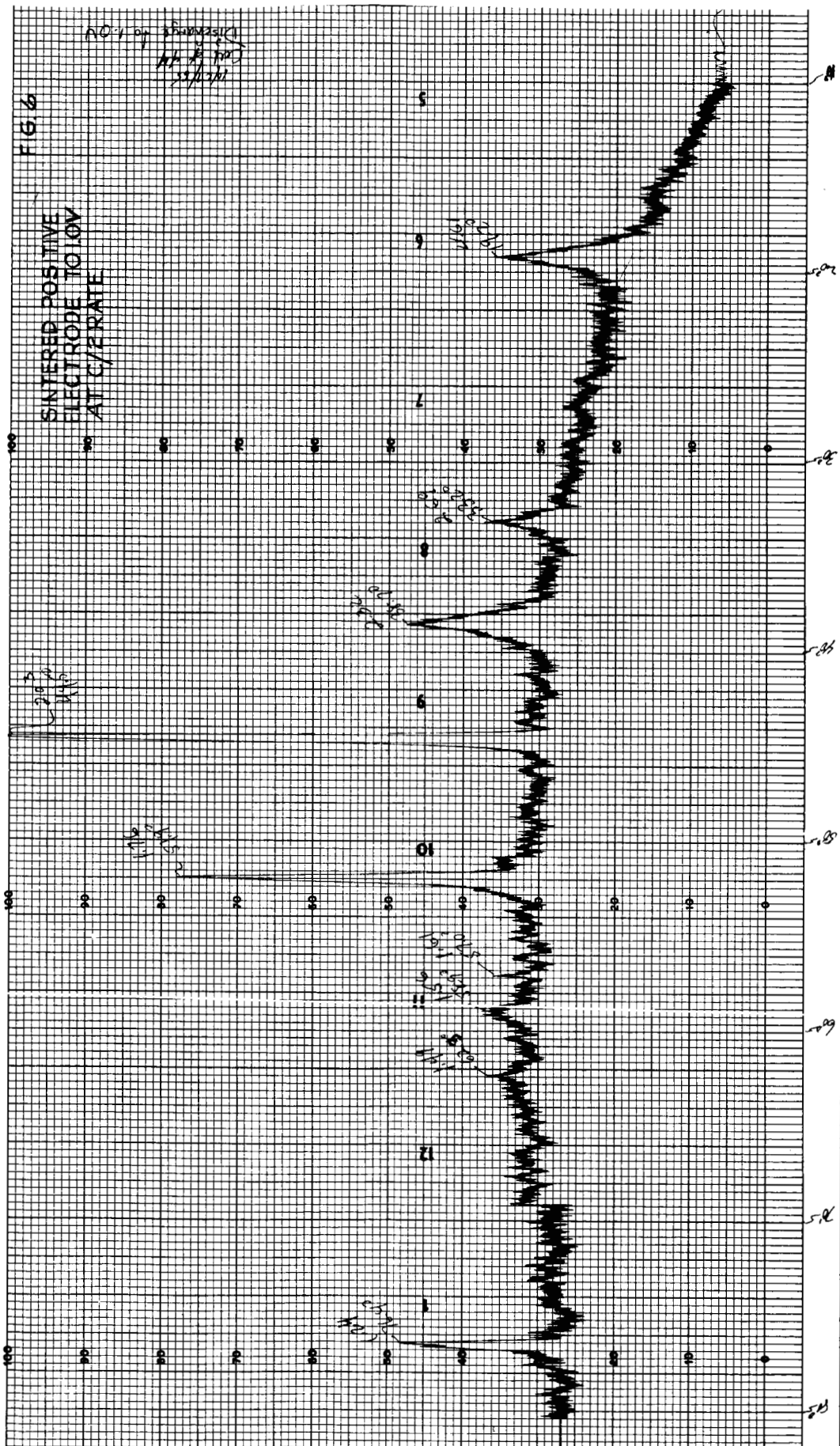
REFERENCES

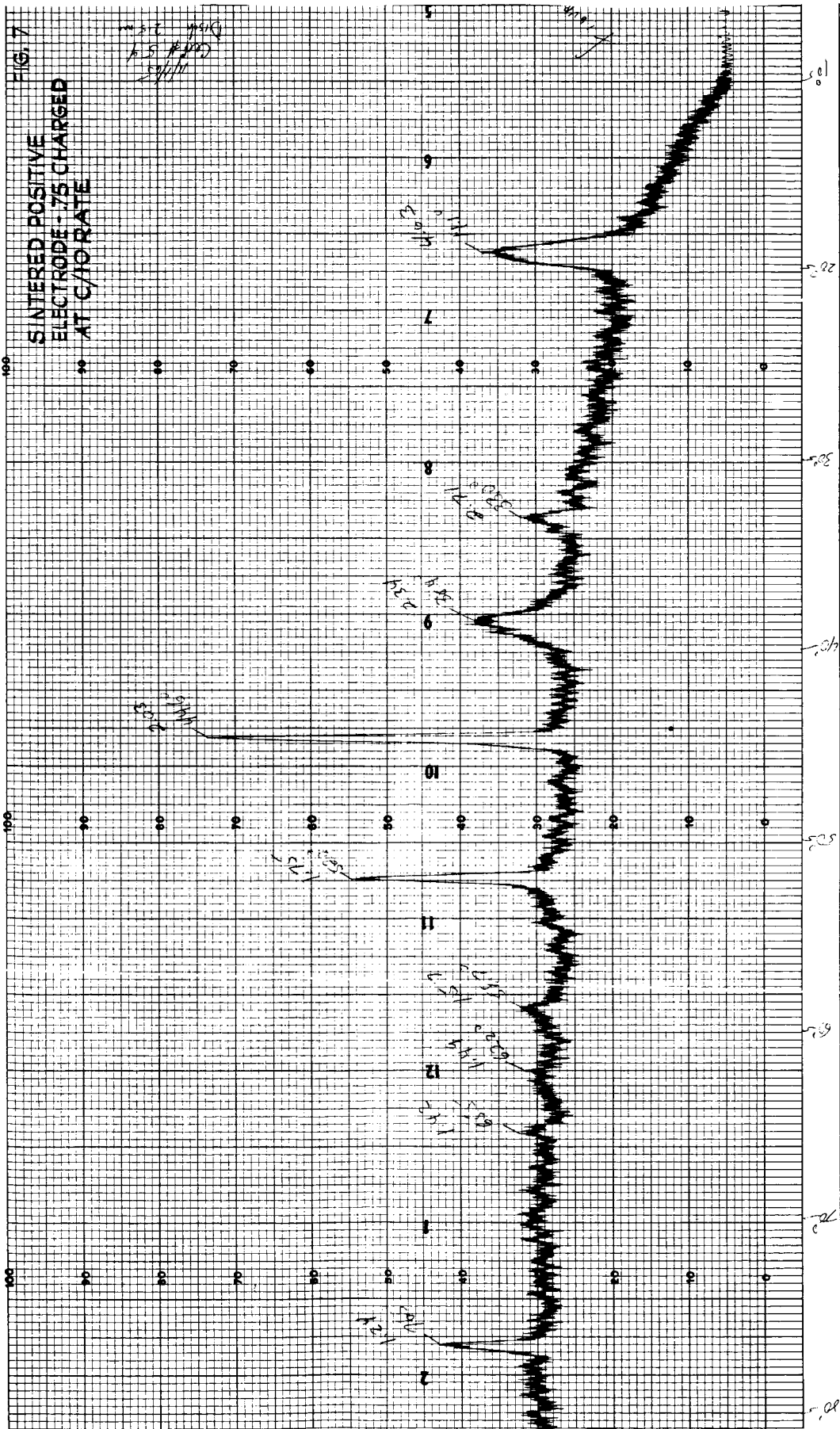
1. Final Report NASA CR-54654, "Investigation of Battery Active Nickel Oxides", Ritterman and Seiger, Contract NAS 3-4178, June 11, 1965.
2. First Quarterly Report, NASA CR-54832, "Investigation of Battery Active Nickel Oxides", Ritterman and Seiger, Contract NAS 3-7620, Sept. 12, 1965.
3. Elements of X-ray Diffraction, B. D. Cullity, Addison-Wesley Publishing Co., Reading, Mass., U.S.A. 1156

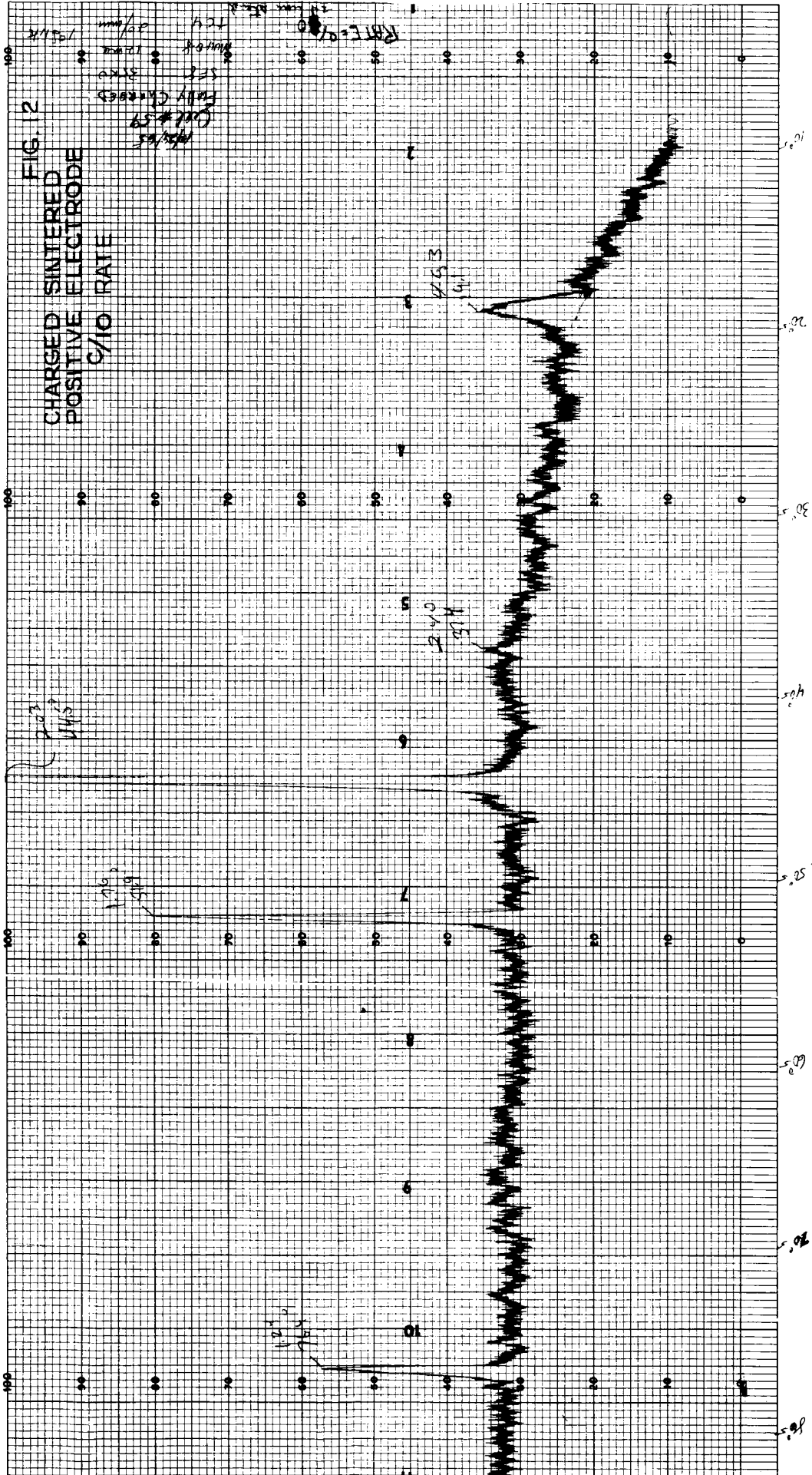


10.5
20.5
30.5
40.5
50.5
60.5
70.5
80.5









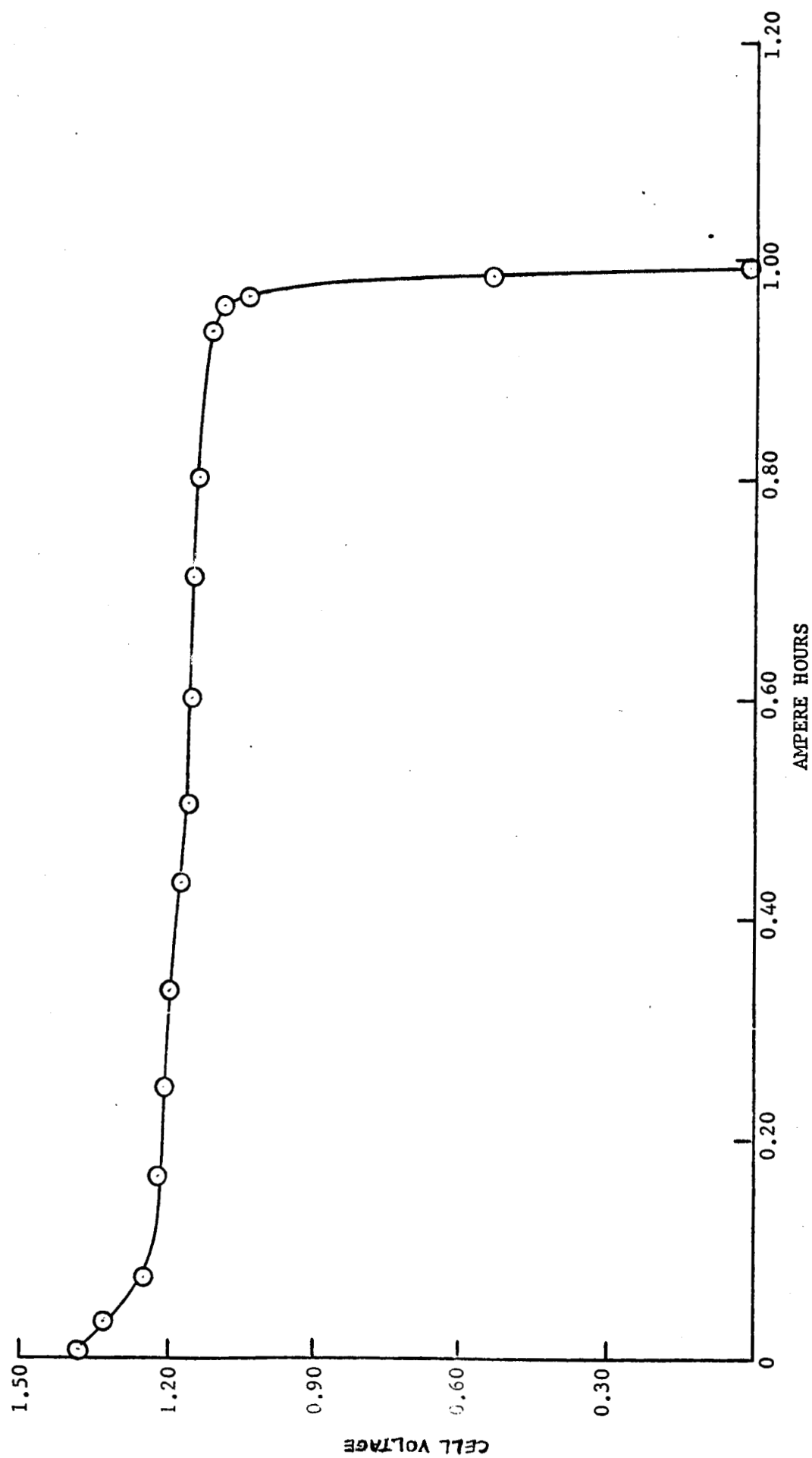


FIGURE 13 TYPICAL DISCHARGE CURVE OF CELL MADE WITH COBALT CONTAINING POSITIVE
DISCHARGED AT C/5 RATE

TABLE I

CAPACITIES OF SINTERED PLATES DISCHARGED AT
400 ma to 1.0 V and 0.0 V

CELL NO.	CYCLE 1		CYCLE 2		CYCLE 3	
	1.0 Volt	0.0 Volt	1.0 Volt	0.0 Volt	1.0 Volt	0.0 Volt
1	.92 AH	.93 AH	.97 AH	1.02 AH	.91 AH	.94 AH
2	.91	.92	.97	.99	.89	.91
* 3	.94	.95	1.01	1.05	.94	.97
* 4	.88	.91	.93	1.03	.88	.95
5	.95	.95	1.08	1.15	1.02	1.06
6	.94	.95	1.07	1.07	.92	.93
* 7	.96	.97	.98	.99	.93	.95
* 8	1.01	1.02	1.03	1.07	.98	1.00
* 9	1.01	1.02	1.05	1.05	.98	.99
* 10	.94	.96	.98	1.01	.92	.94
* 11	.98	.98	1.03	1.05	.95	.96
* 12	.94	.94	1.04	1.05	.98	.99
13	.92	.92	.97	.99	.91	.91
* 14	.90	.90	1.04	1.05	.97	.97
15	1.01	1.02	.99	1.00	.90	.91
* 16	1.04	1.05	.98	.98	.93	.94
17	.93	.94	1.01	1.03	.97	1.00
18	1.05	1.06	.91	.95	.84	.85
19	1.01	1.01	1.05	1.06	1.01	1.01
* 20	.94	1.03	.99	.99	.94	.95
* 21	1.02	1.05	.94	.95	.89	.93
* 22	1.02	1.05	1.00	1.03	.96	1.00

TABLE I - Continued

CELL NO.	CYCLE 1		CYCLE 2		CYCLE 3	
	1.0 Volt	0.0 Volt	1.0 Volt	0.0 Volt	1.0 Volt	0.0 Volt
* 23	.99 AH	1.00 AH	.96 AH	.96 AH	.93 AH	.94 AH
* 24	1.03	1.04	1.01	1.02	.96	.98
* 25	1.05	1.06	1.01	1.02	.98	.99
* 26	1.05	1.06	1.01	1.01	.98	.98
* 27	1.02	1.03	.99	.99	.95	.96
* 28	1.03	1.03	1.01	1.01	.97	.98
29	1.05	1.06	1.01	1.03	.99	1.00
* 30	1.01	1.01	.98	.99	.94	.95

TABLE II

LIST OF "d" SPACINGS AND PEAK HEIGHTS AT VARIOUS STATES
OF CHARGE OF SINTERED POSITIVE ELECTRODES

FIGURE	STATE OF CHARGE	RATE	"d" SPACINGS AND INTENSITIES *			
1	Fully Charged	500 ma	4.61(8)			
2	Fully Charged	500 ma	4.66(10)			
3	One quarter Discharged	500 ma	4.63(13)	2.67(7)	2.32(15)	1.56(3)
4	One quarter Discharged	500 ma	4.73(13)	2.68(5)	2.34(12)	
5	Discharged to 1.0 V	500 ma	4.73(8)	2.72(6)	2.36(10)	1.57(3)
6	Discharged to 1.0 V	500 ma	4.61(18)	2.69(8)	2.32(17)	1.56(5)
7	Discharged to 1.0 V	100 ma	4.66(18)	2.71(7)	2.34(14)	1.58(4)
8	Discharged to 1.0 V	100 ma	4.66(16)	2.71(8)	2.34(12)	1.57(3)
9	One quarter Discharged	100 ma	4.63(18)	2.71(6)	2.34(12)	1.57(3)
10	One quarter Discharged	100 ma	4.61(13)	2.68(4)	2.34(8)	1.56(3)
11	Fully Charged	100 ma	4.66(15)			
12	Fully Charged	100 ma	4.63(13)			

* "d" Spacings in Angstroms; relative intensities are indicated in brackets; nickel lines omitted.

TABLE III
FORMATION DISCHARGE CAPACITIES AT VARIOUS
TEMPERATURES & RATES

DISCHARGE RATE	TEMPERATURE	CAPACITY TO 0.0 V		
		CYCLE 1	CYCLE 2	CYCLE 3
100 ma	25°C	.94 AH	.98 AH	.97 AH
100 ma	25°C	.95	.99	.99
100 ma	25°C	.91	.96	.94
100 ma	25°C	.95	.99	.98
100 ma	25°C	.95	.99	.98
100 ma	25°C	.91	.96	.94
100 ma	25°C	.96	1.00	.99
100 ma	25°C	.94	.99	.98
100 ma	25°C	.94	.98	.97
100 ma	25°C	.91	.98	.94
100 ma	80°C	.70	.70	.72
100 ma	80°C	.67	.68	.70
100 ma	80°C	.75	.77	.75
100 ma	80°C	.68	.67	.69
100 ma	80°C	.72	.72	.73
100 ma	80°C	.76	.77	.78
100 ma	80°C	.77	.77	.79
100 ma	80°C	.79	.77	.79
100 ma	80°C	.75	.77	.76
100 ma	80°C	.59	.60	.61

TABLE III (Continued)

DISCHARGE RATE	TEMPERATURE	CAPACITY TO 0.0 V		
		CYCLE 1	CYCLE 2	CYCLE 3
35 ma	10°C	1.02	1.09	1.05
35 ma	10°C	1.02	1.06	1.05
35 ma	10°C	1.02	1.06	1.11
35 ma	10°C	1.02	1.06	1.00
35 ma	10°C	1.02	1.09	1.05
35 ma	10°C	1.02	1.12	1.05
35 ma	10°C	1.02	1.10	1.05
35 ma	10°C	1.02	1.16	1.11
35 ma	10°C	1.02	1.18	1.12
35 ma	10°C	1.02	.93	.96

TABLE IV

WEIGHT GAIN & DISCHARGE CAPACITY OF PLATES
CONTAINING COBALT

PLATE NO.	WEIGHT GAIN	CAPACITY ON THIRD FORMATION CYCLE	
		1.0 V	0.0 V
Cb-1	3.13 grams	0.91	0.92
Cb-2	3.09	0.90	0.90
Cb-3	2.95	0.87	0.87
Cb-4	2.90	0.85	0.85
Cb-5	2.96	0.86	0.86
Cb-6	3.17	0.92	0.93
Cb-7	3.15	0.92	0.93
Cb-8	2.88	0.83	0.84
Cb-9	2.95	0.87	0.87
Cb-10	3.13	0.92	0.93

TABLE V

SELF DISCHARGE ON STAND AT ROOM & ELEVATED TEMP.

COBALT CONTAINING POSITIVES Vs. CONTROLS

PLATE NO.	INITIAL CAPACITY		2 DAY STAND		7 DAY STAND		TEMP.
	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V	
Control-1	.85 AH	.87 AH			.77AH	.78AH	RT
Control-2	.84	.86			.71	.74	40°C
Control-3	.86	.88			.42	.59	65°C
Cb-5	.85	.88	.81	.81			RT
Cb-10	.91	.91			.83	.88	RT
Cb-2	.88	.89	.80	.81			40°C
Cb-1	.89	.90			.77	.81	40°C
Cb-4	.83	.86	.77	.77			65°C
Cb-3	.84	.86			.71	.75	65°C

Discharged @ 500 ma

TABLE VI

CAPACITY ON DISCHARGE - CYCLING DATA
COBALT CONTAINING PLATES

PLATE	CYCLE 1		CYCLE 2		CYCLE 3		CYCLE 4	
	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0V
Cb-9	.85AH	.88AH	.87AH	.89AH	.91AH	.94AH	.91AH	.94AH
Cb-7	.89	.91	.92	.95	.97	.99	.96	.98
Cb-6	.88	.91	.91	.93	.95	.99	.94	.97
Cb-8	.82	.84	.85	.87	.91	.94	.91	.92

Discharged @ 200 ma